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Electromotive Potential Distribution and Electronic Leak Currents in Working YSZ Based SOC's

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The size of electronic leak currents through the YSZ electrolyte of solid oxide cells have been calculated using basic solid state electrochemical relations and literature data. The distribution of the electromotive potential, of Galvani potential, of concentration of electrons, e , and electron holes, h , was also calculated as these parameters are the basis for the understanding of the electronic conductivity that causes the electronic leak currents. The results are illustrated with examples. The effects of electrolyte thickness, temperature and cell voltage on the electronic leak current density are reported.

Introduction

A solid electrolyte will always possess a finite electronic conductivity. This has given rise to worries about the introduction of high oxygen partial pressures inside the electrolyte and about high leak currents through the yttria stabilized zirconia (YSZ) electrolyte of the solid oxide cell (SOC). Especially, problems may be foreseen in the solid oxide electrolyser cell (SOEC) in case of high cell voltages, which otherwise may be advantageous from an economic point of view, because the higher the cell voltage is, the higher is the hydrogen production rate.

Therefore, it is of considerable interest to get an estimate of which size of electronic current densities that will be present under various electrolysis conditions. The results reported here should be regarded as indicative only, because the precise properties of a zirconia based electrolyte will vary significantly with precise composition, and even low concentrations of some impurities may substantially alter the concentrations and mobility of electron carriers.

Concepts and Assumptions

Figure 1 outlines the basic concepts of electrical potentials in the context of a solid electrolyte. At a position outside a condensed phase in vacuum (see Fig. 1), the so called Volta potential, or outer potential, ψ , is defined as the work per unit charge needed to transport charge from infinity to the point in question. Differences in the Volta potential between two points in vacuum can be determined by the Kelvin probe technique.

The electric potential in the interior of the solid, the Galvani potential, ϕ , deviates from the Volta potential by the surface potential, χ . The *electromotive potential*, π , is

defined as $\pi = -\bar{\mu}_{e^-} / F$, i.e. the electrochemical potential of the electron divided by Faraday's number. This means that the electron concentration is an important contributor to the value of π . For further details, please see ref. (1).

It is important to note that because the electron carrier (e and h) concentration inside the YSZ electrolyte is very low, and the oxide ion concentration is high and constant across the electrolyte, only a gradient in ϕ will cause migration of oxide ions.

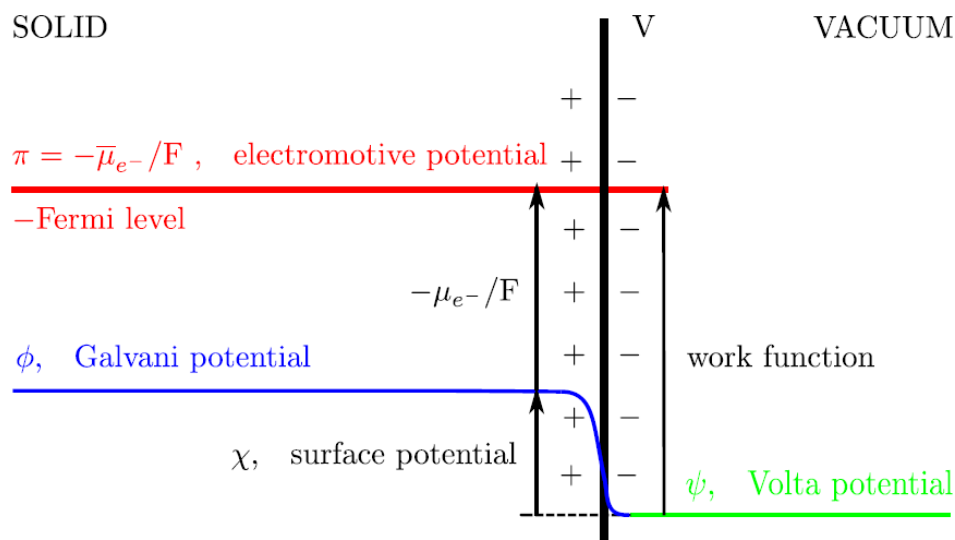


Figure 1. Potentials in a solid conductor relative to the outer electric potential in vacuum.

The necessary equation for calculating the course of the electromotive potential across an SOC was established previously, and using the data for YSZ reported by Park and Blumenthal (2), the distribution of both the electromotive, the Galvani potentials and oxygen partial pressure across the cell was outlined in general (1).

This paper treats cells similar to the Risø DTU type of cells using data from cells measured in solid oxide fuel cell (SOFC) mode (3). The polarization resistances, R_p , are taken as independent of current density. This is a fair approximation for these cells. Further, 1 atm pressure, pure oxygen on the oxygen side, and a $H_2 + H_2O$ mixture with an oxygen potential of -0.9 V (against pure O_2 at 1 bar) on the hydrogen electrode were assumed. The potential of the LSM-YSZ (O_2) electrode is taken as zero, i.e. as the reference.

Then, partly based on data from (3), the following numbers were used as basis for the calculations: At 850 °C $R_{p,Ni-YSZ} = 0.05 \Omega \text{ cm}^{-2}$, the activation energy of the hydrogen electrode $E_{a,Ni} = 0.8 \text{ eV}$, $R_{p,LSM-YSZ} = 0.07 \Omega \text{ cm}^{-2}$, and the activation energy of the oxygen electrode $E_{a,LSM} = 1.1 \text{ eV}$. All specific YSZ data were taken from Park and Blumenthal (2).

Results

The investigated parameters were cell voltage, temperature, and electrolyte thickness. Apart from the curves of electromotive potential distribution, the cell current density (the oxide ion current density) and the electronic leak current densities were calculated.

Figure 1 shows an example of a set of results including π , ϕ , and the concentrations c_e and c_h of the electrons and holes all as a function of the relative distance, x/L , from the interface between the Ni-YSZ (the H_2O/H_2) electrode and the electrolyte. x is the distance and L is the thickness of the electrolyte. It is seen that the electromotive potential, which to a large extent reflects the local concentration of e and h , and thus the "stability" of the YSZ, follows smooth curves, and does not assume any critical value. The concentration profiles of c_e and c_h show that the electrolyte part with the π -values left of the inflection points is predominantly n-type conductor (e is the charge carrier) and on the right side predominantly p-type conductor (h is the charge carrier).

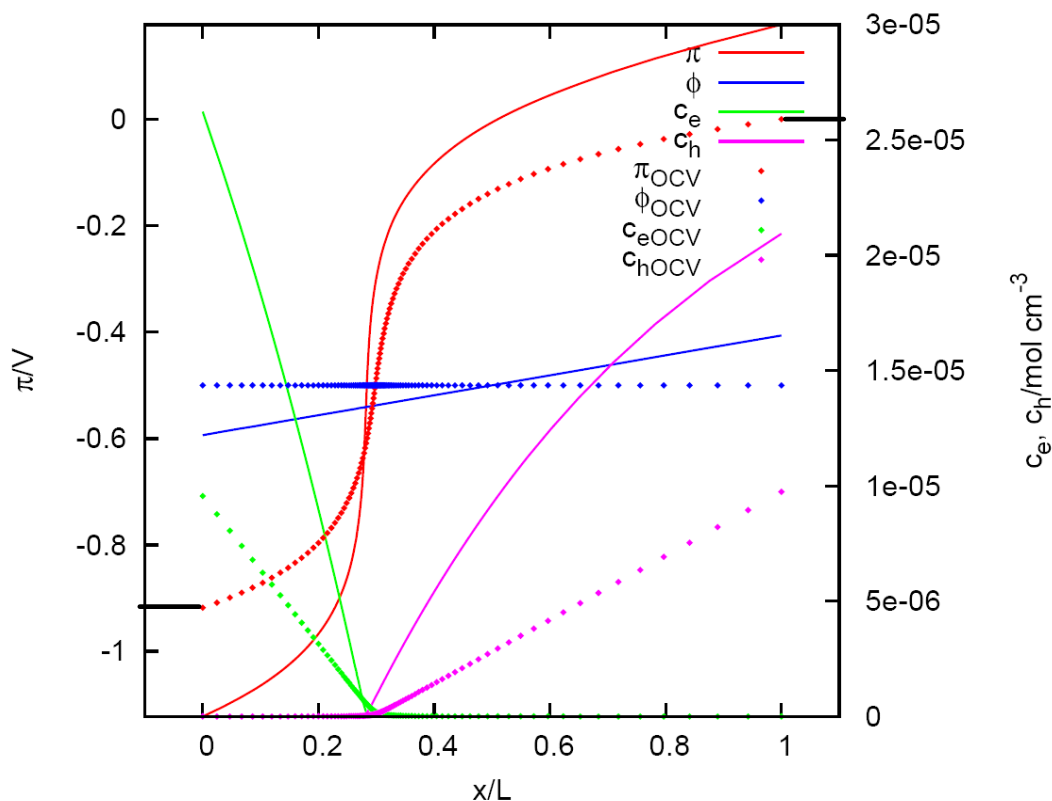


Figure 2. Electromotive voltage, π , and electron and hole concentrations c_e and c_h , as functions of relative distance from the Ni-YSZ/YSZ interface at the open circuit voltage (OCV) of 0.9 V and the thermo-neutral voltage of 1.3 V. YSZ electrolyte thickness $L = 20 \mu\text{m}$, and temperature is 1000°C . The calculated electronic leak current density, $i_{eh} = 16 \text{ mA cm}^{-2}$, and the calculated ionic current density, $i_o = 11 \text{ A cm}^{-2}$ at the cell voltage of 1.3 V. $i_{eh} = 4 \text{ mA cm}^{-2}$ at OCV.

An electronic leak current density, $i_{eh} = 16 \text{ mA cm}^{-2}$ and a cell current density = ionic current density, $i_o = 11 \text{ A cm}^{-2}$ were calculated. The calculated cell current density becomes too high compared to experimental observation, because no mass transport limitations on the steam-hydrogen (Ni-YSZ) side was taken into account. The experimental observed i_o at similar conditions is "only" about 3 A cm^{-2} (4). However, the actual value of i_o is not very important for the value of i_{eh} . The results of the calculations showed that the value of i_{eh} is mainly determined by cell voltage, temperature and electrolyte thickness.

Figure 3 illustrates some of the temperature effects. It is seen that the inflection point is close to the Ni-YSZ interface at 700°C, i.e. most of the electrolyte is p-type conductor. This inflection point moves noticeably towards the oxygen electrode at 1000 °C.

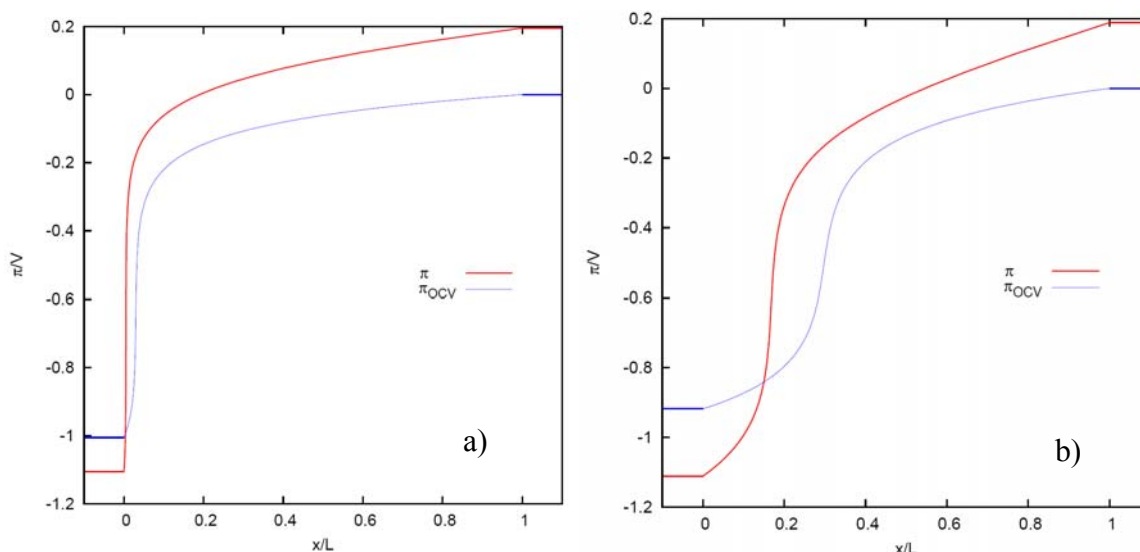


Figure 3. a) 700 °C, $L = 20 \mu\text{m}$, $i_{\text{eh}} = 0.26 \mu\text{A cm}^{-2}$, $i_{\text{O}} = 78 \text{ mA cm}^{-2}$. b) The same conditions as in Fig. 1: 1000 °C, $L = 20 \mu\text{m}$, $i_{\text{eh}} = 16 \text{ mA cm}^{-2}$, $i_{\text{O}} = 11 \text{ A cm}^{-2}$.

The electrolyte thickness of solid oxide cells reported in the literature varies from a few to a few hundreds of μm . Thus, i_{eh} was calculated for the range of 2 to 200 i_{eh} at 4 temperatures, 600, 700, 850 and 1000°C.

Steam electrolysis is an endothermic process. This means that electrolyser cell stack may be self cooling, if it is operated at a suitable voltage. If there is heat available from a non-electric source for evaporation water into steam, the thermo-neutral voltage cell is 1.3 V. If the cell stack also must produce the necessary heat for steam rising, then the voltage needed is close to 1.5 V. In case that there also is some heat loss in the system, then it may be necessary to increase the cell voltage to 1.6 V. Cell voltage higher than 1.6 V will usually not be advisable as this will result in a low energy conversion efficiency, see e.g. (4) and references therein. Thus, the relevant range of cell voltage is from OCV to 1.6 V.

Figure 4 shows the leak current density, i_{eh} , as a function of electrolyte thickness at four temperatures at a cell voltage of 1.3 V. It is worth noting that the ordinate axis is logarithmic. The electron and hole mobility is thermal activated as well as the concentrations, and this causes an increase of i_{eh} of about 500 times when going from 600 to 1000°C. Further, it is observed that $\log i_{\text{eh}}$ decreases approximately linearly with thickness above ca. 100 μm . Below this value, $\log i_{\text{eh}}$ increases progressively with decreasing L .

Figure 5 presents i_{eh} as a function of cell voltage for a 20 μm thick YSZ electrolyte at the same four temperatures as in Figure 4. It reveals that there a linear relationship between $\log i_{\text{eh}}$ and cell voltage exists.

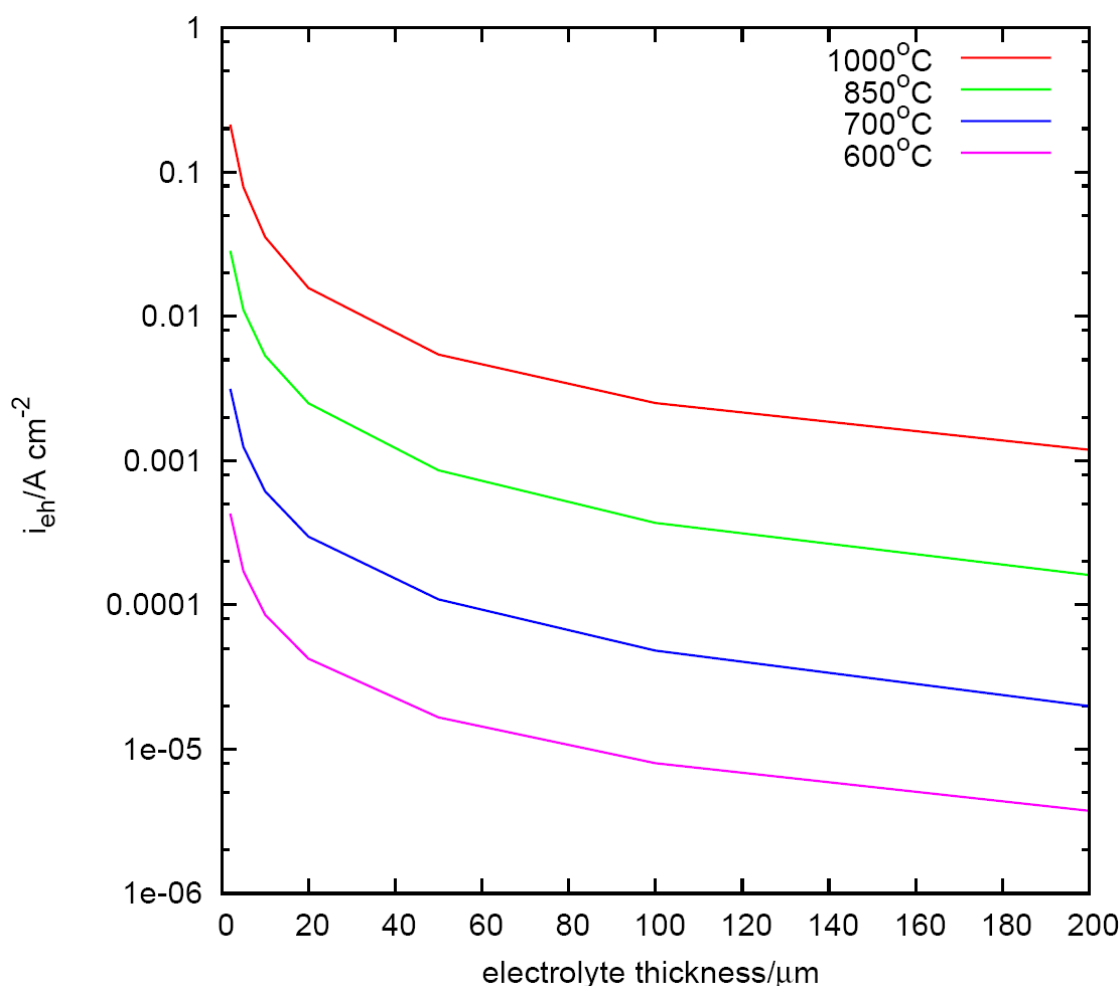


Figure 4. The leak current density, i_{eh} , on log scale as a function of electrolyte thickness at four temperatures at a cell voltage of 1.3 V.

Figs. 4 and 5 together indicate that at a temperature of 1000°C, a thickness of 2 μm , and a potential of 1.6 V will give a substantial leak current density of a few 100 mA cm^{-2} . Thus, this seems to be about or above the limit of what will be technological (economical) acceptable. Even at 850°C, a thickness of 2 μm may give a too high leak current density. However, for 10 μm at 850°C and cell voltage of 1.6 V, i_{eh} will not come much above ca. 10 mA cm^{-2} . As i_o at such conditions will be 1 A cm^{-2} or more, the loss of efficiency due to the electron leakage will be below 1%, which probably will be acceptable.

Concluding Remarks

Calculations of electromotive potentials, electron carrier concentration, and from this, electronic leak current densities through the YSZ electrolyte of a solid oxide electrolyser cell revealed that at temperature of about 850°C or below the leakage will not pose a serious problem as long as a clean YSZ electrolyte is used. However, if the electrolyte is contaminated with e.g. electrode materials during the cell fabrication, then the situation may be significantly worse. Thus, there is a need for more work – experimental as well as modeling – on this subject.

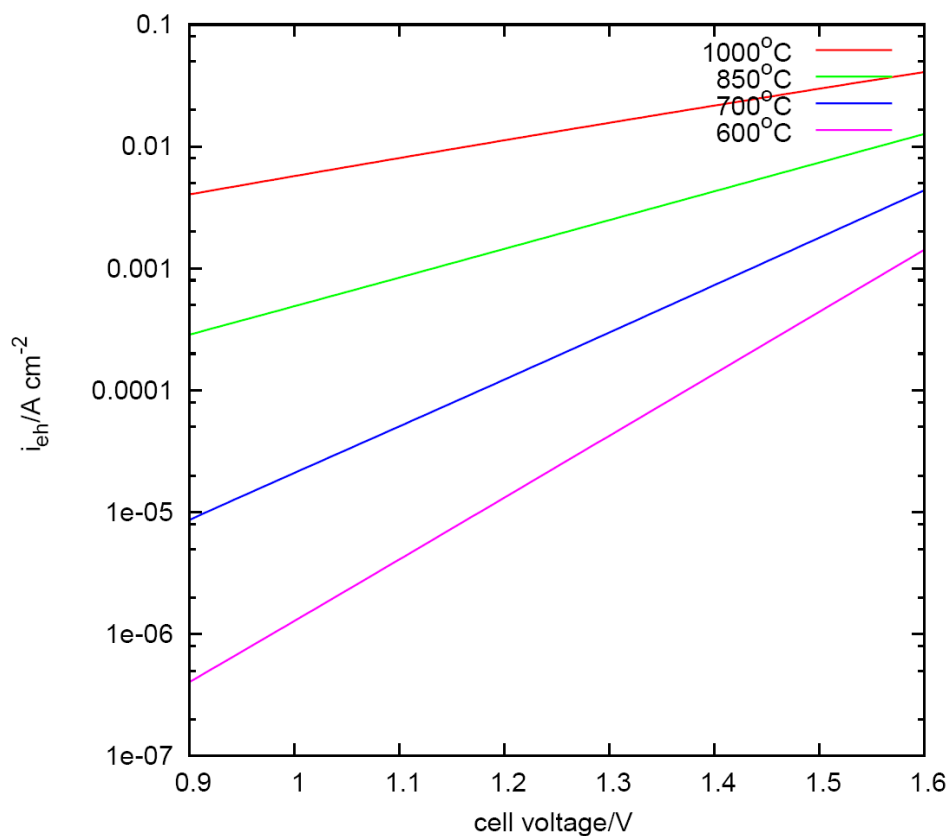


Figure 5. Electronic leak current density, i_{oh} , on a log scale as a function of cell voltage for a 20 μm thick YSZ electrolyte at the same four temperatures as in Figure 4.

Acknowledgments

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